

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Production of Trioxane

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the production of trioxane with a high space-time yield.

The production of trioxane by trimerization of formaldehyde has been known for a long time (cf. Walker, Formaldehyde, 3rd edition, New York, 1964, pages 198 and 199). In general, the synthesis is carried out by heating concentrated aqueous formaldehyde solutions at the boil in the presence of acid catalysts and removing the trioxane-containing synthesis vapor formed from the reactor by distillation. This is usually done by means of a column arranged above the reactor. The trioxane-rich fraction obtained is then extracted and/or worked up by other conventional methods.

In the known processes of this type space-time yields exceeding 175 g of trioxane/kg of formaldehyde per hour cannot be achieved. Similarly, in the process according to Belgian Patent Specification 656,705, which may be regarded as a combination of known processes, the space-time yield is only 58.2 g of trioxane/kg of formaldehyde per hour, the mean residence time of the formaldehyde solution in the reactor being 10 hours.

In a Russian publication (Z.prikland.Chim. 37 (1964), 1620), which deals with the determination of the rate of formation of trioxane, the highest indicated space-time yields are about 175 g of trioxane/kg of formaldehyde per hour.

[Price 4s. 6d.]

It is an object of this invention to provide a process for the production of trioxane with higher space-time yields.

We have found that the space-time yield in trioxane synthesis can be increased to more than 1000 g of trioxane/kg of formaldehyde per hour, i.e. to about 6 times the space-time yield obtained in conventional processes, by altering the process conditions, particularly by increasing the rate of distillation in the reactor while at the same time maintaining a minimum concentration of acid catalysts in the reaction mixture. This is achieved by carrying out the production of trioxane by heating an acid aqueous formaldehyde solution, simultaneous distillative removal of the trioxane-containing product vapor from the reactor and subsequent fractional distillation of the product vapor in a column, in such a way that a concentration of 2 to 25% by weight of a mineral acid or a catalytically equivalent concentration of a different acid catalyst is maintained in the synthesis mixture; the mean residence time of the aqueous formaldehyde solution in the reactor is from 2 minutes to 2 hours, advantageously from 10 to 100 minutes, and the product vapor is introduced into the middle section of a column having at least 5 theoretical trays, from whose upper section a trioxane-rich mixture and from whose lower section a mixture of formaldehyde and water is withdrawn.

Thus, the process according to the invention is characterized by a specific arrangement of apparatus, by the concentration of acid in the synthesis mixture and by the very short mean residence time of the aqueous formaldehyde solution in the reactor, that is to say, by a combination of several features.

The synthesis mixture in the reactor

usually contains, apart from the acid catalysts, about 30 to 70%, particularly 50 to 65%, by weight of formaldehyde or paraformaldehyde, about 70 to 30%, particularly 50 to 35%, by weight of water, and, if desired, the usual additives, e.g. antifoam. It is heated in the reactor at the boil together with the acid catalysts at atmospheric, sub-atmospheric or superatmospheric pressure. Conventional reactors may be used, e.g. stirred vessels. Circulation vaporizers are particularly suitable as reactors, because a large amount of heat is required for achieving the necessary high rate of distillation. According to the invention, the synthesis mixture should contain from 2 to 25%, particularly 4 to 15%, by weight of a mineral acid, particularly a strong mineral acid. Concentrations of 5 to 15% by weight of a strong mineral acid have proved to be particularly suitable. Preferred mineral acids are sulfuric acid, perchloric acid, toluenesulfonic acid, and phosphoric acid. Instead of the said amounts of mineral acids, catalytically equivalent amounts of other known catalysts may be used for the production of trioxane. By the term 'catalytically equivalent amount' is meant an amount which from the same starting materials and under the same reaction conditions produces the same product at the same reaction velocity as the stated amounts of mineral acids do. In general, it is not the type but only the amount, i.e. the overall catalytic activity, of the acid catalyst used that is critical for achieving the high space-time yields in accordance with the invention. Obviously only such catalysts should be used which are less volatile than the synthesis mixture. Examples of other known acid catalysts, whose catalytic activity is known or may easily be determined, are acid inorganic salts, such as potassium hydrogen sulfate and zinc chloride; aliphatic and aromatic sulfonic acids, such as p-toluenesulfonic acid and 1,5-naphthalenedisulfonic acid; and in particular acid ion exchangers, such as commercial cation exchange resins having  $\text{SO}_3\text{H}$  radicals, e.g. crosslinked polystyrenesulfonic acid.

In the process according to the invention the mean residence time of the aqueous formaldehyde solution in the reactor should be from 2 minutes to 2 hours, advantageously 10 to 100 minutes, preferably 10 to 50 minutes. The mean residence time of the aqueous formaldehyde solution in the reactor may easily be determined from the ratio of the amount of reaction mixture in the reactor to the amount of distillate leaving the reactor per unit time.

The trioxane-containing synthesis vapor leaving the reactor is introduced into the middle section of a column having at least 5 theoretical trays either as such or in con-

densified form, if possible avoiding reflux into the reactor. The point of entry into the column should be so arranged that the stripping section of the column has at least 2 theoretical trays and is large enough to remove substantially all of the trioxane and that at the bottom of the column an aqueous formaldehyde solution having a low trioxane content, which is advantageously less than 2%, is obtained from the stripping section. Equipment for destroying any foam present may be arranged between the reactor and the column.

The column usually comprises a vaporizer, a stripping section, a rectifying section and, if desired, a dephlegmator. It should have a separating effect of at least 5 theoretical trays. The number of trays is governed mainly by the desired degree of separation in the column. Columns having 5 to 50, particularly 10 to 25, theoretical trays have proved to be suitable for the process according to the invention.

In the lower part of the column a mixture of formaldehyde and water is obtained which may contain small amounts of other substances, e.g. trioxane and formic acid. In general the trioxane content should not be more than 2%, particularly not more than 0.5%.

From the upper part of the column a trioxane-rich mixture of trioxane, formaldehyde and water is withdrawn which may contain small amounts of acetals, esters, acids or alcohols. In general the trioxane content of the mixture is approximately 40 to 70%. If the same amount of water as that introduced into the reactor together with fresh formaldehyde is distilled off together with the trioxane at the head of the column, the mixture of formaldehyde and water which is obtained at the bottom of the column may be directly recycled to the reactor in liquid form or as a vapor. This embodiment of the process is therefore particularly suitable for continuous operation; it also prevents excessive concentration of the synthesis mixture in the reactor and the formation of insoluble substances, such as paraformaldehyde. If however less water is distilled off in the column than is introduced into the reactor together with fresh formaldehyde, there is obtained at the bottom of the column a formaldehyde-water mixture which contains less formaldehyde than the starting material and which therefore cannot be recycled to the reactor until it has been concentrated in an appropriate manner.

The space-time yields which can be achieved by the process according to the invention and which range between about 500 and 1000 g of trioxane/kg of formaldehyde per hour are very surprising because the features of the process according to the invention are in no way suggested by

the prior art. In the prior art literature the formation of trioxane from formaldehyde has in general been referred to as slow. In contrast to this, the process according to the invention implies that the formation of trioxane proceeds very rapidly. In the prior art literature an increase in the amount of acid added to the synthesis mixture has been regarded as disadvantageous, and in German Patent Specification 1,135,491 (column 1) it is stated that an increase in the amount of mineral acids results in more intense side reaction and in a lower trioxane yield. On the other hand, in the process according to the invention the addition of a larger amount of acid has proved to be advantageous; the increase in the amount of acid should however be attended by a shortening of the mean residence time of the formaldehyde solution in the reactor if very high yields are desired. Thus, in the case of sulfuric acid concentrations of from 6 to 12% by weight mean residence times in the reactor of from 10 to 20 minutes have found to be advantageous for obtaining reaction products having a low content of by-products, such as methyl formate, and at the same time for achieving favorable space-time yields of about 500 to 1000 g of trioxane/kg of formaldehyde per hour.

The process according to the invention has the particular advantage that it is very suitable for continuous operation with recycling of the formaldehyde-water mixture obtained at the bottom of the column to the synthesis unit of the plant, i.e. the reactor.

The invention is further illustrated by the following examples, in which parts and percentages are by weight unless otherwise specified. Parts by volume bear the same relation to parts by weight as the liter to the kilogram.

#### EXAMPLE 1

80 parts of concentrated aqueous technical-grade formaldehyde solution (approx. 60%) and 5 parts of sulfuric acid are introduced into the reactor. The synthesis mixture is heated at the boil and the vapor formed is passed into the middle section of a distillation column whose stripping and rectifying sections each have 10 theoretical trays. At the same time concentrated aqueous formaldehyde solution is allowed to flow into the reactor from a reservoir at such a rate that there is always 80 parts of reaction mixture in the reactor.

The vapor of the synthesis mixture is separated in the column into a fraction having a high trioxane content and a fraction having a low trioxane content. In the course of 24 hours there is obtained at the top of the column 1460 parts of a mixture consisting of 36.6% of trioxane, 38.1% of water, 23.8% of formaldehyde, 0.9% of

methanol and 0.25% of low-boiling substances, such as methylol and methyl formate.

At the bottom of the column a formaldehyde-water mixture is obtained which comprises 57.0% of formaldehyde, 41.8% of water, 1.6% of trioxane and 0.18% of methanol. This mixture is continuously recycled direct to the reactor. The mean residence time of the aqueous formaldehyde solution in the reactor is approx. 80 minutes and the space-time yield is 465 g of trioxane/kg of formaldehyde per hour.

#### EXAMPLE 2

77 parts of concentrated aqueous formaldehyde solution (approx. 60%) and 3 parts of sulfuric acid are placed in the reactor. The mixture is heated at the boil and the vapor leaving the reactor is passed into the middle section of a column having a separating effect of about 15 to 20 theoretical trays. At the same time concentrated aqueous formaldehyde solution is allowed to flow into the reactor at such a rate that there is always 80 parts of synthesis mixture in the reactor.

The vapor of the synthesis mixture are separated in the column into a fraction having a high trioxane content and a fraction having a low trioxane content. A mixture of 39.1% of trioxane, 37.5% of water, 21.7% of formaldehyde, 1.28% of methanol and 0.46% of low-boiling constituents is obtained at the top of the column. In the course of 24 hours 3520 parts of trioxane-rich reaction mixture is obtained.

A formaldehyde-water mixture comprising 62.2% of formaldehyde, 37.7% of water, 0.26% of trioxane and 0.31% of methanol is obtained as bottoms. It is continuously recycled direct to the reactor. The mean residence time of the aqueous formaldehyde solution in the reactor is 14.5 minutes and the space-time yield is approx. 1119 g. of trioxane/kg of formaldehyde per hour.

#### EXAMPLE 3

360 parts of a 60% aqueous formaldehyde solution (specific gravity approx. 1.17) and 40 parts of concentrated sulfuric acid are placed in a circulation vaporizer having a capacity of 400 parts by volume. 1111 parts per hour of aqueous solution is distilled off, while at the same time 1111 parts of 60% aqueous technical-grade formaldehyde solution (methanol content 1 to 2%) is allowed to flow in. The distillate is introduced into a bubble-cap tray column having 40 theoretical trays at the height of the 10th theoretical tray. 317 parts of a mixture containing 65.5% of trioxane, 9.4% of formaldehyde, 21.1% of water, 2.2% of methanol and 1.8% of other organic by-products is obtained at the head of the column.

980 parts of a mixture containing 55% of formaldehyde, 0.1% of trioxane, 0.4% of methanol and 44.5% of water is with-



drawn at the bottom. The mixture is concentrated in a vacuum vaporizer to a formaldehyde content of 60% and introduced into the reactor feed. The mean residence time of the aqueous formaldehyde solution in the reactor is 25 minutes and the space-time yield is approx. 820 g of trioxane/kg of formaldehyde per hour.

#### EXAMPLE 4

10 336 parts of a 60% aqueous formaldehyde solution and 64 parts of concentrated sulfuric acid are placed in a stirred distillation vessel. The concentration of sulfuric acid in the reaction mixture is 16%.  
 15 In the course of 1 hour 460 parts of a mixture containing 16% of trioxane and 38.4% of formaldehyde is distilled off from the reactor, while at the same time 460 parts of a 53 to 55% aqueous formaldehyde solution is allowed to flow in. The  
 20 distillate contains 0.3% of methanol, 0.9% of methyl formate and 0.4% of methylol in addition to formaldehyde and trioxane. As in Example 3, the vapors of the distillate  
 25 are introduced into a bubble-cap tray column having 40 theoretical trays at the height of the 10th theoretical tray. The mean residence time of the aqueous formaldehyde solution in the reactor is 48 minutes and the  
 30 space-time yield is approx. 350 g of trioxane/kg of formaldehyde per hour.

#### EXAMPLE 5

340 parts of a 60% aqueous formaldehyde solution and 60 parts of polystyrene-sulfonic acid (Dowex 50 X 4 200-400 mesh, Dowex being a Registered Trade Mark of Dow Chemical Company) are placed in a stirred distillation vessel. In the course of  
 35 1 hour 1000 parts of a mixture containing 17% of trioxane, 41% of formaldehyde and 1% of by-products is distilled off, while at the same time the same amount of a 60% aqueous formaldehyde solution is allowed to flow in. As described in Example  
 40 3, the vapors are introduced into a column for separation of the trioxane. The mean residence time of the aqueous formaldehyde solution in the reactor is 40 minutes and

the space-time yield is approx. 710 g of trioxane/kg of formaldehyde per hour. 50

#### WHAT WE CLAIM IS:—

1. A process for the production of trioxane by heating an aqueous formaldehyde solution in the presence of an acid catalyst, simultaneous distillative removal of the trioxane-containing product vapor from the reactor and subsequent fractional distillation of the product vapor in a column, wherein a concentration of 2 to 25% by weight of a mineral acid or a catalytically equivalent concentration of a different acid catalyst is maintained in the synthesis mixture, the mean residence time of the aqueous formaldehyde solution in the reactor is from 2 minutes to 2 hours and the product vapor is introduced into the middle section of a column having at least 5 theoretical trays, a trioxane-rich mixture being withdrawn from the upper section of said column and a mixture of formaldehyde and water from the lower section of said column. 55 60 65 70

2. A process as claimed in claim 1 wherein the mean residence time of the aqueous formaldehyde solution in the reactor is from 2 to 100 minutes. 75

3. A process as claimed in claim 1 or 2 wherein the concentration of mineral acid in the synthesis mixture is from 4 to 15% by weight.

4. A process as claimed in any one of claims 1 to 3 wherein the mixture of formaldehyde and water withdrawn from the lower section of the column is recycled to the reactor either direct or after having been concentrated. 80 85

5. A process for the production of trioxane substantially as described in any of the foregoing Examples.

6. Trioxane when obtained by the process as claimed in any one of claims 1 to 5. 90

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